Dissolution Mechanism of Fluorine in Aqueous Solution from Fluorine Containing Synthetic Slag

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The behavior of dissolution of fluorine from the fluorine containing synthetic slag was clarified by the shaking test under various experimental conditions. The fluorine containing minerals were cuspidine, fluorapatite and fluorite. The amount of fluorine dissolved from the slag increased with an increasing of the concentration of fluorine in the slag and an decreasing of the size of slag particles. The amount of fluorine dissolved from the slag could be estimated from the size distribution of slag particle and the concentration of slag for the shaking test. The amount of fluorine dissolved from the slag decreased with an increasing of the basicity of slag and the concentration of alumina. The amount of fluorine from the slag increased with increasing the cooling rate during solidification because the slag became amorphous. The dissolution of fluorine from the slag was controlled by the mass transfer in the liquid layer which was formed near the surface of slag.

KEY WORDS: slag; fluorine; dissolution; shaking test.

1. Introduction

Recycling and utilization of the slag produced in steel-making process are important and it is necessary to lessen the burden on environment by decreasing of disposal of reclamation and to decrease the production cost.1) In steel-making process, the fluorite might be contained in slag to enhance the fluidity of flux, and then the dissolution of fluorine from that slag was concerned. As there is a possibility that the amount of dissolution of fluorine is restricted in the future, it is indispensable to establish the stabilization technology of fluorine from the fluorine containing slag.2–5)

Then, it is important to understand the behavior of dissolution of fluorine from the slag.

Therefore, in this study, the shaking tests using the synthetic slag were done to clarify the dissolution behavior of fluorine from the slag and to obtain the guideline for decreasing the amount of fluorine from the slag.

2. Experimental Procedures

2.1. Test Sample

To clarify the behavior and mechanism of dissolution from slag containing fluorine, the important factors such as the composition of slag, the state whether melted completely or not before solidification and the cooling rate during solidification of slag have to be taken into consideration. In this study, however, the experiments of dissolution of fluorine from synthetic slag were carried out under constant cooling rate during solidification of slag and the mechanism of dissolution of fluorine was examined.

The reagent chemicals were mixed and put in a dense magnesia crucible, and then were melted at 1 973 K for 30 min and solidified at a fixed cooling rate of 0.05 to 10 K·s\(^{-1}\) from 1 973 K to 973 K. The furnace was put in the vacuum vessel, and the regents were melted and solidified under argon gas atmosphere. By doing so, the composition change of slag was prevented during melting and cooling.

The cooling rate was chosen so that observed in the plant, because the morphology of fluorine containing mineral phase and the ratio of crystal to amorphous depended on the cooling rate during solidification. Furthermore, to study the influence of cooling rate during solidification on slag characteristic, the rapid solidification by pouring into copper mold from crucible and the mild cooling by turning off of furnace power under molten state were chosen. The cooling rate during solidification at these conditions was obtained from the temperature–time curve in the experiments where the thermocouple was immersed in the slag.

The dissolution of fluorine from slag strongly depends on the distribution of particle size, that is, specific surface area of slag. Therefore, the distribution of slag particle size was fixed in such a way that the distribution is nearly the same as that of plant slag which was crushed by using jaw crusher. After crushing, the slag was riddled by sieves machine for 20 min using six kinds of sieves of which had opening screen from 0.1 to 2.0 mm, and the distribution of particle size of slag was controlled by mixing these riddled slags.

2.2. Experimental Method for Dissolution of Fluorine

The evaluation of dissolution of fluorine from slag was followed by the shaking test which was based on the
Environmental Agency Notice 46.

Table 1 gives the experimental condition for shaking test. The diameter of slag for shaking test is 2.0 mm or less in diameter and the weight of slag is 50 g. The initial pH value of the aqueous solution for shaking test is adjusted to 5.8–6.3 and the volume of aqueous solution is 500 mL, which corresponds to ten times of slag weight. The shaking time is 6 h, and the frequency of shaking test is 200 times per minute. The dissolved fluorine from slag was analyzed according to the JIS method in which the aqueous solution being filtered using a membrane filter with open pore size of 0.45 μm was analyzed by absorption spectroscopy.

### 3. Results and Discussion

To clarify the behavior of dissolution of fluorine from slag, the experiments were made as functions of slag diameter, composition, cooling rate during solidification of slag, shaking time, initial pH value of aqueous solution and temperature of aqueous solution for shaking.

#### 3.1. Characteristics of Slag for Shaking Test

##### 3.1.1. Diameter of Slag

The change of weight and composition of slag before and after shaking test was examined at different slag diameters. Table 2 shows slag composition and fluorine containing mineral phase obtained by X-ray diffraction analysis at different slag diameters. No composition change was observed before and after shaking test in each diameter of slag. Moreover, the distribution of particle size of slag before and after shaking test did not change during shaking test, as shown in Fig. 1. The fluorine containing mineral phase of a cuspudine (3CaO·2SiO2·CaF2) was identified by the X-ray diffraction analysis. It seems that the amount of dissolution of fluorine from slag depends on the distribution of slag particle, that is, the specific surface area of slag particle. Then, the amount of dissolution of fluorine from each particle size of slag was measured for the slag containing different concentrations of fluorite as shown in Table 3.

Figure 2 shows the relationship between amount of dissolution of fluorine from slag and diameter of slag particle. The amount of fluorine dissolution from slag increases with increasing the concentration of fluorite in slag and decreasing diameter of slag particle. It is thought that the amount of fluorine dissolution is governed by the slag of 0.1 mm or less in diameter because the amount of fluorine in aqueous solution from the slag of 0.1 mm or less in diameter is higher than that in larger diameters. Therefore, it is indispensable to control the distribution of particle size of slag for evaluating the dissolution of fluorine from slag.

The hydrate products after shaking test were studied by Suito and Inoue in detail and a lot of kinds of fluorine containing hydrates observed in the filtered residue such as CaO–SiO2–H2O gel.

Figure 3 shows the relationship between the amount of fluorine in aqueous solution from slag and concentration of fluorite in slag under various diameters. When the slag diameter was the same, the fluorine in aqueous solution from slag increased linearly as the concentration of fluorite increased. From these results, it is said that the dissolved amount of fluorine in aqueous solution from slag depends on both the distribution of particle size and the concentration of fluorite in slag. In other words, the amount of fluorine dissolution can be estimated as a function of diameter of slag and concentration of fluorite.

The equation of fluorine content in aqueous solution from slag obtained from Fig. 3 can be derived and this equation is applicable when the composition of slag corresponds from sample F2 to F13 and shaking time is 6 h.

\[
F = \sum_d f_d \times W_d \quad \text{..........................(1)}
\]

\[
f_d = A_d C_0 + B_d \quad \text{................................(2)}
\]

where \(F\) is fluorine content in aqueous solution from slag (mg·L\(^{-1}\)), \(C_0\) is concentration of fluorite in slag (mass%), \(W_d\) is fraction of slag of \(d\) mm in diameter, and constant \(A_d\) and \(B_d\). These values are listed in Table 4.

The relationship between predicted value of fluorine obtained by the equation and the experimental results by shaking test is shown in Fig. 4, indicating that the predicted val-

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Table 1. Shaking condition by the Environmental Agency Notice 46.

<table>
<thead>
<tr>
<th>Slag</th>
<th>Weight</th>
<th>Diameter (mm)</th>
<th>Aqueous solution</th>
<th>Shaking test</th>
<th>Analysis (JIS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50 g</td>
<td>≤ 2.0</td>
<td>500 ml</td>
<td>6 h</td>
<td>Method</td>
</tr>
<tr>
<td></td>
<td></td>
<td>mm</td>
<td></td>
<td>Frequency 200 cycle/min</td>
<td>Absorption spectroscopy</td>
</tr>
</tbody>
</table>

Table 2. Slag composition (mass%) and fluorine containing mineral phase before and after shaking test.

<table>
<thead>
<tr>
<th>Diameter (mm)</th>
<th>CaO</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>P2O5</th>
<th>TiO2</th>
<th>Fe2O3</th>
<th>F</th>
<th>F containing mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>≤0.1</td>
<td>46.3</td>
<td>22.9</td>
<td>4.6</td>
<td>5.7</td>
<td>5.5</td>
<td>3.4</td>
<td>3.1</td>
<td>3CaO·2SiO2·CaF2</td>
</tr>
<tr>
<td>0.1-2.0</td>
<td>46.5</td>
<td>22.7</td>
<td>4.3</td>
<td>5.8</td>
<td>5.4</td>
<td>2.9</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>0.25-0.5</td>
<td>46.7</td>
<td>22.8</td>
<td>4.4</td>
<td>5.9</td>
<td>5.4</td>
<td>2.9</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>0.5-1.0</td>
<td>46.2</td>
<td>22.3</td>
<td>4.4</td>
<td>5.7</td>
<td>5.4</td>
<td>3.1</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>1.0-1.4</td>
<td>46.1</td>
<td>22.5</td>
<td>4.6</td>
<td>5.7</td>
<td>5.4</td>
<td>3.1</td>
<td>3.1</td>
<td></td>
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<tr>
<td>1.4-2.0</td>
<td>46.0</td>
<td>22.8</td>
<td>4.6</td>
<td>5.6</td>
<td>5.5</td>
<td>2.9</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>After</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>5.6</td>
<td>5.4</td>
<td>3.7</td>
<td>3.2</td>
<td>3CaO·2SiO2·CaF2</td>
</tr>
<tr>
<td>0.1-2.0</td>
<td>45.3</td>
<td>23.1</td>
<td>5.9</td>
<td>5.6</td>
<td>5.4</td>
<td>3.7</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>0.25-0.5</td>
<td>46.3</td>
<td>23.3</td>
<td>5.8</td>
<td>5.8</td>
<td>5.6</td>
<td>3.1</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>0.5-1.0</td>
<td>46.5</td>
<td>23.4</td>
<td>5.5</td>
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<td>3.1</td>
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<td>23.5</td>
<td>5.4</td>
<td>5.7</td>
<td>5.5</td>
<td>3.4</td>
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<td>5.8</td>
<td>5.8</td>
<td>3.4</td>
<td>3.1</td>
<td></td>
</tr>
</tbody>
</table>
values are corresponding well to the measured values. From these results, it is understood that fluorine in aqueous solution from slag is able to be controlled with particle size of slag.

In the following shaking test, the distribution of slag particle was fixed in order to eliminate the influence of slag size on fluorine dissolution.

3.1.2. Composition of Slag

It is thought that the fluorine in aqueous solution dissolved from slag depends on the kind of fluorite containing mineral phase. The fluorine containing mineral phase changes depending on not only the concentration of fluorite but also the concentration of Al₂O₃, SiO₂ or P₂O₅ etc.

The shaking test was done by using slags with the composition listed in Table 5, and the effect of composition on amount of fluorine dissolved from slag was examined. As shown in Table 5 indicating the results of both X-ray diffraction and electron microprobe analysis for the fluorine containing mineral phases, the kind and the fraction of fluorine containing mineral phases are changed with composition of slag. In this study, the fluorine containing mineral phases were cuspidine, fluorapatite (Ca₅F(PO₄)₃) and fluorite (CaF₂), under the cooling rate during solidification of 5.0 × 10⁻² K·s⁻¹.

The relationship between fluorine content in aqueous solution from slag and composition of slag is shown in Fig. 5, in which the change of kind and fraction of fluorine containing mineral phases with composition of slag are also shown. Figure 5(a) shows the relationship between fluorine
content in aqueous solution and basicity of CaO/SiO₂ ratio. Though the amount of fluorine dissolution is not changed in the range of CaO/SiO₂ between 1.0 and 2.0, that of fluorine is decreased when the basicity is 3.0. The fluorine containing mineral phase is changed depending on the basicity, that is, the mineral phase is cuspidine when the basicity is 1.0 and 2.0, and fluorite when the basicity is 3.0.

Figure 5(b) shows the relationship between amount of dissolved fluorine and concentration of alumina. The higher the concentration of alumina is, the lower the amount of fluorine is. Though the fluorine containing mineral phase is cuspidine when the concentration of alumina is low, the cuspidine and fluorapatite coexist when the concentration of alumina is high.

The influence of concentration of phosphoric oxide on dissolution of fluorine from slag is shown in Fig. 5(c) indicating that the higher the concentration of phosphoric oxide, the lower the amount of fluorine in aqueous solution from slag. The fluorine containing mineral phase changes depending on the concentration of phosphoric oxide. The mineral phase is only cuspidine when the concentration of phosphoric oxide is low, and the mineral phase becomes the coexisting phase of cuspidine and fluorapatite when the concentration of phosphoric oxide is high.

The relationship between amount of fluorine and concentration of FeO is shown in Fig. 5(d). Fluorine is not changed even if the concentration of FeO is changed. The fluorine containing mineral phase is cuspidine in the studied range of FeO concentration.

From these results, it is thought that the amount of fluorine in aqueous solution from slag is changed depending on both kind and fraction fluorine containing mineral phase. Therefore, the fluorine containing mineral phases confirmed in this study were synthesized with reagents, and the relationship between amount of dissolved fluorine and synthetic mineral phase was examined.

Figure 6 shows the relationship between fluorine containing mineral phase and amount of fluorine in aqueous solution by shaking test after 6h. The fluorine content is measured by the shaking test using the mineral phase 0.1 mm or less in diameter. The pH value of aqueous solution was in the range from 11.7 to 12.0. The amount of fluorine is changed depending on the kind of fluorine containing mineral phase, that is, the amount of dissolved fluorine decreases in the order of cuspidine>fluorapatite>fluorite. The reason why the amount of dissolved fluorine was changed by the basicity and composition shown in Fig. 5 can be interpreted by the change of the kind and the fraction of fluorine containing mineral phase.

To decrease the amount of fluorine dissolved from slag, it is thought that the fluorapatite phase is preferable by increasing the basicity or the concentration of alumina.

3.1.3. Cooling Rate during Solidification of Slag

Though it is known that the dissolved amount of fluorine ion from amorphous soil is larger than that of crystalline soil, it is not certain with respect to the dissolution of fluorine from slag. For this reason, the amorphous and the crystalline slags were made under various cooling rate during solidification, and the dissolution behavior of fluorine from slag was examined. The results of X-ray diffraction analysis of slags obtained by using the sample F6 under various cooling rate during solidification are shown in Fig. 7. As
the cooling rate during solidification increased in order of $5.0 \times 10^{-2}$, $6.0 \times 10^{-2}$, 2.3 and $10 \text{ K} \cdot \text{s}^{-1}$, the peak of X-ray diffraction analysis of slag becomes broad and unclear. So, the slag becomes amorphous at higher cooling rate.

**Figure 8** shows the change of fluorine amount in aqueous solution with cooling rate during solidification. It is seen that the amount of fluorine increases with increasing the cooling rate, because the slag becomes amorphous at higher cooling rate.

To control the dissolution behavior of fluorine from slag, it is necessary to consider the influence of cooling rate during solidification.

### 3.2 Conditions of Shaking Test

To examine the influence of conditions of shaking test on dissolution of fluorine from slag, the slag sample F6 in Table 3 was used. The cooling rate during solidification of sample F6 was $5.0 \times 10^{-2} \text{ K} \cdot \text{s}^{-1}$ and the distribution of particle size was regulated in such a way as shown in Fig. 1.

#### 3.2.1 Shaking Time

To promote the utilization of fluorine containing slag, it is necessary to evaluate the time dependency of fluorine dissolution from slag, though the time of shaking test is fixed on 6 h in the case of the Environment Agency Notice 46.

**Figure 9** shows the relationship between fluorine content in aqueous solution and cooling rate during solidification. The shaking test was done by using slag with the particle size $<0.1$, $1.4/2.0 \text{ mm}$ and that shown in Fig. 2 to clarify the effect of the shaking time. When the distribution of particle size of slag was regulated, the fluorine from slag increased with increasing shaking time until 24 h. The amount of fluorine in aqueous solution from slag using single particle size range of 0.1 mm or less in diameter is larger than that of slag with the particle size of 1.4/2.0 mm.

Though the fluorine content of the slag with the size of 1.4/2.0 mm increases with increasing shaking time, the amount of fluorine for a given shaking time is smaller than that of slag with the regulated distribution of particle size shown in Fig. 2. These results suggest that the larger specific surface area significantly influences the amount of fluorine dissolution from slag.

#### 3.2.2 The pH Value

The relationship between pH value of aqueous solution for shaking test and shaking time is also shown in Fig. 9 by using the slag of which distribution of particle size is regulated. Though the pH value of aqueous solution before shaking test is 5.8–6.3, the pH value increases initially to a large degree, but the degree of increase is small during the shaking test.

The pH value of aqueous solution changed in the shaking test and the amount of fluorine dissolved from slag also changed. Therefore, it seems that the amount of fluorine is influenced by an initial pH value of aqueous solution for shaking test. The relationship between pH value before and after shaking tests was examined by using the aqueous solution whose pH value was smaller than 7.0.

**Figure 10** shows the relationship between pH value before and after shaking tests. The pH value increases after shaking test in any case and also changed by an initial pH value before shaking test. When an initial pH value before shaking test is larger than about 4.0, the pH value after shaking test increases to more than 7.0. As the slag is easily dissolved in acid solution, the amount of slag dissolution is higher and the influence of pH value is larger.

**Figure 11** shows the change of amount of fluorine from slag with an initial pH value before shaking test. With decreasing the initial pH value of aqueous solution before
shaking test, the amount of fluorine dissolved from slag increases. This is because the amount of fluorine depends on the change of pH value during shaking test. However, when an initial pH value is larger than 4.0, the difference of the amount of fluorine by the pH value is small.

3.2.3. Cycle of Shaking and Temperature of Aqueous Solution

To understand the mechanism of dissolution of fluorine from slag, the shaking test has been made by changing the cycle of shaking and the temperature of aqueous solution. The experimental apparatus used is shown in Fig. 12. The temperature was measured by the thermocouple immersed in the shaking water and the rubber heater wrapped around the polyethylene bottle was used to control the temperature. The results are shown in Fig. 13. The amount of fluorine in aqueous solution from slag increases with an increase in the cycle of shaking and temperature.

If the dissolution of fluorine from slag is controlled by the solution of slag, the rate of solution depends on the Reynolds number \( (Re = \frac{ru}{\mu}) \), namely, with an increase of Reynolds number the rate of solution of slag increases. Both the density \( \rho \) and the viscosity \( \mu \) of water depend on the temperature, and with increasing the temperature of water both \( \rho \) and \( \mu \) values decrease. Moreover, because the temperature dependency of \( \mu \) is larger than that of \( \rho \), the Reynolds number increased with increase temperature of water. As the representative length which corresponds to the diameter of bottle \( d \) is constant and the velocity of water depends on the cycle of shaking, the Reynolds number was normalized based on the case of 200 cycle/min and 298 K.

Figure 14 shows the relationship between amount of fluorine dissolved from slag and normalized Reynolds number. Even if the temperature of water and the cycle of shaking are changed, the amount of fluorine from slag is proportional to the normalized Reynolds number, and the amount of fluorine dissolved from slag increases with increasing the normalized Reynolds number.

From these results, the amount of fluorine dissolved from slag is seemed to be controlled by the mass transfer in the liquid layer formed near the surface of slag. Therefore, the parameter of predicting the equation for the amount of fluorine from slag is only determined by the shaking time.

4. Conclusions

The behavior of dissolution of fluorine from the fluorine containing slag has been clarified by the shaking test using
the synthetic slags. The shaking tests were done by using the slags made under various conditions. From these experimental results, the following guideline for decreasing the amount of fluorine from the slag was obtained.

1) The amount of dissolved fluorine from the slag depended on the diameter of slag for a given slag composition. The amount of fluorine in aqueous solution increased with decreasing the diameter of slag. The amount of dissolution of fluorine from the slag was able to be predictable as a function of the diameter of slag.

2) The amount of dissolved fluorine from the slag increased with increasing the concentration of fluorite in the slag.

3) The fluorine containing mineral phase changed by changing the basicity and the composition of slag. When the concentration of fluorite in the slag was the same, the amount of dissolved fluorine increased with decreasing the basicity and increasing the concentration of alumina.

4) With an increase in the cooling rate during solidification of slag, the amount of dissolved fluorine from the slag was increased, because the slag became amorphous.

5) The dissolution of fluorine from the slag was estimated by the rate controlling step of mass transfer within the liquid layer formed near slag surface.

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